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(54) Surface-roughened film and method for fabricating thereof.

(57) A surface-roughened film having good transparency/exceptional clarity and high lubricity and useful as a photoengraving material, a label, packaging film, a magnetic recording film, and a clear film is formed of a composition comprising thermoplastic polyester resin (a) a thermoplastic resin (b) having a glass transition temperature higher than that of the thermoplastic polyester resin (a), a critical surface tension which differs by more than 0.1 dyne/cm from that of the thermoplastic polyester resin (a), and a melt viscosity at a temperature of 280°C and shear rate of 10<sup>2</sup> sec<sup>-1</sup>, of 500 to 50,000 poise; and optionally a particulate inorganic compound (c), and has protuberances cored with the thermoplastic resin (b) on at least one surface thereof.

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## BACKGROUND OF THE INVENTION

## Technical Field of the Invention

5     This invention relates to a surface-roughened film and methods for fabricating such a film. The surface-roughened film has good transparency/exceptional clarity and high lubricity so that it is useful for a photoengraving material, a label, a packaging film, a magnetic recording film, and a clear film.

## Description of the Prior Art

10     A polyester film represented by a polyethylene terephthalate film exhibits exceptional physical and chemical properties, so that it can be applied for various products such as a magnetic recording material, a wrapping material, an electrical material, a sensitized material, and many photographic materials.

15     For example, it is well known that the polyester films dominate the market share in the magnetic tape industries and the lubricity (slip characteristics) of the film significantly affects operativity in manufacturing process or succeeding working process of the films and, in turn, affects the quality of intermediate or end products.

20     In order to obtain this lubricity, such a method is generally employed to previously incorporate particulate inorganic compounds into a polymer to generate irregularity on the surface by means of drawing. Such a technique is proposed in, for example, the Japanese Patent Unexamined Prepublication No.63-137927, where it is difficult to uniformly disperse fine particles because the particulate inorganic compounds tend to aggregate or agglomerate with each other. With respect to this, other technique disclosed in, for example, the Japanese Patent Unexamined Prepublication No.63-66222 employs a method such that the particulate inorganic compounds are added to the polymer on its polymerization.

25     Recently, transparent films are in great demand and the higher transparency is required for the polyester film, which is so called "thick-walled film", having film thickness in the range of 50 to 200  $\mu\text{m}$  which is for use in a microfilm, an electrophotograph, an X-ray photograph, a diazo print, a slidefilm (filmstrip) for an overhead projector (OHP), a label, and a laminated film. Generally, a thick film absorbs and scatters more light compared with a thin film, upon its transmission through the film, so that the transparency may essentially be degraded though the thick-walled film having high transparency also have been commercially available.

30     However, as described below, such films are relatively not easy to be handled. More particularly, films are fabricated generally in various steps such as a drawing step, a rolling step, a slitting step, and a working step before to be used as the end products. It is indispensable to prevent blocking of the film or to add the lubricity to the film for facilitating handling thereof when passing through these steps. Troublesome handling in these steps results in defected end products. In order to facilitate this handling, the film is usually incorporated with particulate inert materials of inorganic compound to cause adequate irregularity on the film surface and thereby preventing blocking of the films. In addition, incorporation of such particles contributes to the proper lubricity between films and, in turn, to prevention of troubles accompanying with rolling-up of films used as the intermediates or end products. The above-mentioned lubricity of the film is improved with reducing troubles in various processes by increasing the volume of added particles, whereas it is disadvantageous in that the resultant lower transparency of the film will cause some loss of desired optical characteristics and visual appearance of the film.

35     On the other hand, it is necessary for increasing desired transparency of the film to reduce the volume of the added particulate inert materials of inorganic compound, resulting in lower lubricity of the film and causes many handling troubles in various steps. One example of such handling troubles caused by the lower lubricity is that small protuberances are generated on the film surface of a rolled film upon rolling up the films after drawing. Excessive generation of such protuberances may cause not only bad appearance of the film but also considerable damages to the film used in industries where precision and accuracy for the film transparency are required for optical, photographic, or graphical purposes. Thus, it is difficult to satisfy both transparency and lubricity, which are the antipodal properties of the film.

40     In addition, in the above-mentioned method where the particulate inert materials of inorganic compound are added, its productivity of film is exceedingly low because of clogging of a screen with the inorganic particles in filtering process on melt film formation, while a screen having the larger mesh size may allow some foreign matters to be incorporated into the film, which is disadvantageous in that such a film is often broken down on its drawing. Further, even a small amount of inorganic particles being added may cause wearing of T-die lip or T-die blade if melt film formation is last over a long time. Accordingly, to overcome the above-mentioned problem has long been desired. The incorporated particles also affect to lifetime of a knife used in slitting process or other cutting process of the film, that is, exceedingly short-wearing knife will necessitates frequent replacement of the knife resulting in reduced productivity. In addition, the film with some additive or foreign matters

Useful  
as mag. rec.  
film.

is disadvantageous when being used for a magnetic tape or other magnetic recording media, because a head of a recorder may be worn by its incorporated particles.

Conventionally, most of the solutions have been proposed for the above-mentioned "thick-walled film" by means of compromising between transparency and lubricity of the film rather than consisting them together. For example, the compromise solutions are to highly control processing conditions with an expensive plant investment to a processing device and to reduce processing speeds or take-up speeds.

However, it would be highly desirable also for a thick-walled transparent film to essentially provide both transparency and lubricity of the film with improving a device for fabricating such a film in view of the necessity for increasing processing speeds and improving productivity.

# Object of the Invention

An object of the present invention is to provide a polyester film having, in particular, good transparency/exceptional clarity and high lubricity with respect to the above-mentioned problems.

## Summary of the Invention

According to a first aspect of the present invention, a surface-roughened film is comprising a composition (I) containing a thermoplastic polyester resin (a) in the range of 97 to 99.99 wt.%; and a thermoplastic resin (b) in the range of 0.01 to 3 wt.% of which glass transition temperature is higher than that of the thermoplastic polyester resin (a) and the critical surface tension thereof is more than 0.1 dyne/cm difference from that of the thermoplastic polyester resin (a), and melt viscosity is, at a temperature of 280°C and shear rate of 10<sup>2</sup>sec<sup>-1</sup>, in the range of 500 to 50,000 poise, or is a laminated film laminated with other polymers such that said composition (I) is formed on at least one surface thereof characterized in that micro-protruberances cored with the thermoplastic resin (b) are generated on the surface of the film or that of the laminated film.

Preferably, a three dimensional center plane average roughness (SRa) of the surface-roughened film is within a range of 0.005 to 0.05 μm, and a three dimensional ten point average roughness (SRz) is within a range of 0.06 to 0.4 μm.

According to a second aspect of the present invention, a surface-roughened film is comprising a composition (II) containing a thermoplastic polyester resin (a) in the range of 96.9 to 99.9899 wt.%; a thermoplastic resin (b) in the range of 0.01 to 3 wt.%; and particulate inert materials of inorganic compound (c) in the range of 0.0001 to 0.1 wt.%, of which average particle size is in the range of 0.2 to 4.0 μm, or is a laminated film laminated with other polymers such that said composition (II) is formed on at least one surface thereof characterized in that microprotruberances cored with the thermoplastic resin (b) are generated on the surface of the film or that of the laminated film.

Preferably, the three dimensional center plane average roughness (SRa) of the surface-roughened film is within a range of 0.007 to 0.07 μm, and the three dimensional ten point average roughness (SRz) is within a range of 0.1 to 0.5 μm.

In the first and second aspects of the present invention, it is preferable that a refractive index of the thermoplastic resin (b) is in the range of 1.45 to 1.68 and mean dispersed particle size is in the range of 0.01 to 1.0 μm.

According to a third aspect of the present invention, a method for making a surface-roughened film characterized by comprising a step of drawing by a factor of one and half in at least one direction, an undrawn film comprising a composition (I) containing a thermoplastic polyester resin (a) in the range of 97 to 99.99 wt.%; and a thermoplastic resin (b) in the range of 0.01 to 3 wt.%, or a laminated film laminated with other polymers such that said composition (I) is formed on at least one surface thereof, at the glass transition temperature of the thermoplastic polyester resin (a) through the range of the glass transition temperature of the thermoplastic resin (b).

According to a fourth aspect of the present invention, a method for making a surface-roughened film characterized by comprising a step of drawing by a factor of one and half in at least one direction, an undrawn film comprising a composition (II) containing a thermoplastic polyester resin (a) in the range of 96.9 to 99.9899 wt.%; a thermoplastic resin (b) in the range of 0.01 to 3 wt.%; and particulate inert materials of inorganic compound (c) in the range of 0.0001 to 0.1 wt.%, of which average particle size is in the range of 0.2 to 4.0 μm, or is a laminated film laminated with other polymers such that said composition (II) is formed on at least one surface thereof, at the glass transition temperature of the thermoplastic polyester resin (a) through the range of the glass transition temperature of the thermoplastic resin (b).

## Detailed Description of the Preferred Embodiments

*Polyester*  
The compositions of thermoplastic polyester resin according to the present invention is based on a combination of mixed residues of aromatic dicarboxylic acid, aliphatic diol and/or alicyclic diol.

5 The following are exemplified species containing the aromatic dicarboxylic acid: 1, 4-benzenedicarboxylic acid (terephthalic acid), 1,3-benzenedicarboxylic acid (isophthalic acid), and naphthalene dicarboxylic acid. The aromatic rings of these aromatic dicarboxylic acids may be substituted by halogens, alkyls or other substituents.

10 The following are exemplified species containing the aliphatic diol and/or alicyclic diol: 1,2-ethanediol (ethylene glycol), bis(2-hydroxyethyl) ether (diethylene glycol), 1,2-propanediol (propylene glycol), 1,3-butanediol (butylene glycol), 2,2-dimethyl-1,3-propanediol (neopentyl glycol), and cyclohexylene dimethanol. It is possible to contain two or more of combined aliphatic diol and/or alicyclic diol.

*Polyester*  
*A = PET*  
15 The following are exemplified species of the thermoplastic polyester resin (a): polyethylene terephthalate (PET), polybutylene terephthalate (PBT), polyethylene-2,6-naphthalate (PEN), poly-1,4-cyclohexylene dimethylene terephthalate (PCT) and poly-p-ethylene oxybenzoate (PEOB). These resins satisfy requirements for the polyester resin for films in an economic and efficient manner. It is noted that a glass transition temperature (hereinafter, referred as Tg) of the thermoplastic polyester resin (a), which is important relative to Tg of the thermoplastic resin (b), can be measured by means of a differential scanning calorimetry (DSC) technique. *Tg*  
20 The value of this glass transition temperature is generally 70°C for the PET, 50°C for the PBT, 120°C for the PEN, 95°C for the PCT, and 60°C for the PEOB. It is readily understood that other components may be incorporated into these thermoplastic polyester resin as a copolymerized components to such a degree that the film formation is not interfered. It is also readily understood that the thermoplastic polyester resin (a) may be formed with a composition of PET and the thermoplastic polyester resin (a) other than PET.

25 There is no restriction regarding to a molecular weight of the thermoplastic polyester resin (a) used in the present invention and only the necessity is the film formation ability thereof. However, it is preferable that the intrinsic viscosity thereof is not less than 0.4(dl/g), measured at a temperature of 25°C being solved in a mixed solvent of phenol/tetrachloroethane of 1:1 (weight ratio).

*Resin b*  
*Tg = Tg30*  
30 The thermoplastic resin (b) used in the present invention has Tg higher than that of the thermoplastic polyester resin (a) and the critical surface tension which is more than 0.1 dyne/cm difference from that of the thermoplastic polyester resin (a). Such Tg and critical surface tension is determined so as to satisfy the following requirements. Composition formed by the thermoplastic polyester resin (a) as a matrix component (continuous phase) and the thermoplastic resin (b) as an island component (dispersed phase) as a result of molten mixture of the thermoplastic polyester resin (a) and the thermoplastic resin (b). This mixture is extruded in the form of a film and then drawn into the surface-roughened film. Thus, the present invention will not be achieved when the critical surface tension of the thermoplastic resin (b) is equal or approximate to that of the thermoplastic polyester resin (a) because of the compatibility between the thermoplastic polyester resin (a) and the thermoplastic resin (b). In addition, lower Tg of the thermoplastic resin (b) compared with that of the thermoplastic polyester resin (a) causes the thermoplastic resin (b) to be deformed into smooth plane when the thermoplastic polyester resin (a) is drawn. This means that the thermoplastic resin (b) is hindered to be cored (i.e. the island components of the thermoplastic resin (b) are formed as a core in the thermoplastic polyester resin (a) because of non-compatibility therebetween) and the desired micro-protuberances on the film surface will not be generated. There is more than 0.1 dyne/cm difference in the critical surface tensions of the thermoplastic polyester resin (a) and the thermoplastic resin (b), and more preferably, is more than 0.5 dyne/cm. In addition, Tg of the thermoplastic polyester resin (a) is preferably 10°C higher than, and more preferably, 20°C higher than Tg of the thermoplastic resin (b). *higher Tg Molten mixture*

*Properties of Resin b*  
35 It is necessary that the melt viscosity of the thermoplastic resin (b) at the temperature of 280°C and the shear speed of 10<sup>2</sup>sec<sup>-1</sup> is in the range of 500 to 50,000 poise, and is preferable in the range of 1,000 to 30,000 poise. When the melt viscosity is lower than 500 poise, then smaller particles of the thermoplastic resin (b) are dispersed in the matrix of the thermoplastic polyester resin (a), which results in insufficient lubricity of the film. On the other hand, when the melt viscosity is higher than 50,000 poise, then larger particles of the thermoplastic resin (b) are generated resulting in insufficient transparency of the film. The refractive index of the thermoplastic resin (b) is preferably in the range of 1.45 to 1.68. The film with the refractive index of less than 1.45 exhibits the film with insufficient transparency. The transparency is improved as the refractive index approaches to 1.68. The refractive index of more than 1.68 may be applicable while the thermoplastic resin having such viscosity of more than 1.68 is not readily available. In the surface-roughened film according to the present invention, the thermoplastic resin (b) of the island component is dispersed in the thermoplastic polyester resin (a) of the matrix component. In this event, it is preferable that the thermoplastic resin (b) is dispersed in the form of approximately sphere particles. Preferably, the average dispersion particle size is in the range of 0.005 to 2.0  $\mu$ m.

*roughness (S from 6)  
0.001-0.1 μm*

μm, and more preferably, in the range of 0.01 to 1.0 μm.

In the surface-roughened film according to the present invention, the micro-protuberance are generated on the surface of the film with thermoplastic resin (b) being cored thereof when particulate inert materials of inorganic compound (c) described below are not contained. Preferably, surface roughness of the film is in the range of 0.001 to 0.1 μm, and more preferably, in the range of 0.005 to 0.05 μm, measured by the three dimensional center plane average roughness (SRa) and in the range of 0.01 to 0.8 μm, and more preferably, in the range of 0.06 to 0.4 μm, measured by the three dimensional ten point average roughness (SRz). The lubricity of the film is not sufficient with SRa of smaller than 0.001 μm and with SRz of smaller than 0.01 μm while the transparency of the film is not sufficient with SRa of larger than 0.1 μm and with SRz of larger than 0.8 μm. It is noted that SRa represents the mean distance of the peak and valley from the center plane where the total area of the island is equal to that of the matrix on the film surface. SRz represents the distance between the average of first to fifth highest peaks and the average of first to fifth deepest valleys.

The thermoplastic resin (b) used in the present invention exemplifies polystyrene, polymethyl methacrylate, polycarbonate, polyarylate, polyethersulphone, amorphous nylon, amorphous polyurefin, and maleimide copolymeric resin

For use in the above-mentioned amorphous nylon, polyamides are adequate which contain, as its copolymerized components, 5-tert-butyl 1,3-benzenedicarboxylic acid (5-tert-butyl isophthalic acid),

1,3-trimethyl-3-phenylindan-3',5-dicarboxylic acid,

3-aminomethyl-3,5,5-trimethyl-cyclohexylamine,

1,3-diaminocyclohexane,

m-xylylendiamine,

1,3-bis(aminomethyl) cyclohexane,

2,4,4-trimethyl hexamethylenediamine,

bis(4-aminocyclohexyl) methane,

bis(4-amino-3-ethylcyclohexyl)methane.

Such polyamide can be obtained by means of well-known polycondensation technique in combination with polyamide forming components such as

1,2-diaminoethane(ethylenediamine),

1,4-diaminobutane(tetramethylenediamine),

1,6-diaminohexane(hexamethylenediamine),

phenylenediamine,

hexanedioic acid(adipic acid),

decanedioic acid(sebacic acid),

cyclohexanedicarboxylic acid,

1,3-benzenedicarboxylic acid(isophthalic acid),

1,2-benzenedicarboxylic acid(phthalic acid),

1,4-benzenedicarboxylic acid (terephthalic acid),

naphthalenedicarboxylic acid,

ε-aminocaproic acid,

ω-aminododecanoic acid,

aminobenzoic acid,

ε-caprolactam and ω-laurolactam.

Preferably, Tg of the amorphous nylon is at least 10°C higher than, and more preferably, at least 20°C higher than Tg of the thermoplastic polyester resin (a). The surface-roughening may be more effectively made with the higher Tg. However, it is preferable that Tg is not higher than 200°C with respect to processability on melt molding.

The maleimide copolymeric resin used in the present invention contains at least groups of monomers of maleimide and aromatic vinyls, and if necessary, also contains unsaturated dicarboxylic anhydride monomers and other copolymerizable monomers.

The following are representative of monomers of such maleimides:

maleimide,

N-methylmaleimide,

N-ethylmaleimide,

N-propylmaleimide,

N-hexylmaleimide,

N-cyclohexylmaleimide,

N-phenylmaleimide,

N-tolylmaleimide,

N-(phenylhalide)maleimide,  
 N-(alkyl phenyl)maleimide,  
 N-(nitrophenyl)maleimide,  
 N-(hydroxyphenyl)maleimide,  
 5 N-naphthylmaleimide,  
 $\alpha$ -chloro-N-phenylmaleimide, and  $\alpha$ -methyl-N-phenylmaleimide.

The following are representative of the aromatic vinyl monomers: styrene,  $\alpha$ -methylstyrene, vinyltoluene, t-butyl styrene, and styrene halide.

The following are representative of the unsaturated dicarboxylic anhydride monomers: maleic anhydride  
 10 (2,5-furandione), methyl maleic anhydride, 1,2-dimethyl maleic anhydride, ethyl maleic anhydride, and phenyl maleic anhydride.

The other copolymerizable monomer is acrylic monomer, which represents: methylacrylate, methylmethacrylate, ethylacrylate, ethylmethacrylate, butylacrylate, butylmethacrylate, hexylacrylate, hexylmethacrylate, cyclohexylacrylate, cyclohexylmethacrylate, decylacrylate, decylmethacrylate, octadecylacrylate, octadecylmethacrylate, hydroxyethylacrylate, hydroxyethylmethacrylate, methoxyethylacrylate, methoxyethylmethacrylate,  
 15 glycidylacrylate and glycidylmethacrylate.

*maleimide composition*  
 The maleimide copolymeric resin used as the thermoplastic resin (b) in the present invention exemplifies by comprising maleimide monomer of 5 to 50 mol%, aromatic vinyl monomer of 30 to 90 mol%, unsaturated dicarboxylic anhydride monomer of 0 to 50 mol% and other copolymerizable monomers of 0 to 50 mol%. With the aromatic vinyl monomer of more than 90 mol%, Tg of the maleimide copolymeric resin will be unpreferably reduced. With the maleimide monomer of more than 50 mol% or the unsaturated dicarboxylic anhydride monomer of more than 50 mol%, it is unpreferably difficult to industrially manufacture homogeneous copolymeric resin. It is also unpreferable that the other copolymerizable monomer is more than 50 mol% because Tg of the maleimide copolymeric resin is reduced and the heat stability of the composition is reduced.  
 20

The maleimide copolymeric resin used in the present invention can be made by means of well-known free-radical polymerization technique. The other producing method for the maleimide copolymeric resin is to react the copolymer of the unsaturated dicarboxylic acid anhydride monomer, the aromatic vinyl monomer and, if required, other copolymerizable monomer group with ammonia or primary amine to make all or a part of anhydride groups thereof into imides. The maleimide copolymeric resin can be manufactured by means of this reaction into imides between the polymers having the anhydride group and amine compounds according to methods disclosed in, for example, Japanese Patent Examined Publication Nos. 61-26938 and 62-8456.  
 25

*T<sub>g</sub> > T<sub>g</sub><sup>a</sup>*  
 The maleimide copolymeric resin used in the present invention has Tg which is 10°C higher than, and more preferably, 20°C higher than that of the thermoplastic polyester resin (a). If Tg of the maleimide copolymeric resin is equal to or lower than that of the thermoplastic polyester resin, the drawing of the film made of their composition will cause plastic deformation of the maleimide copolymeric resin therein and fine irregularities on the surface of the film will not enough to be generated. With the maleimide copolymeric resin having such lower Tg, the resulting polyester film has insufficient lubricity.  
 30

There is no restriction regarding to the molecular weight of the maleimide copolymeric resin used in the present invention, and such molecular weight is well enough to such a degree that melt viscosity of 500 to 50,000 poise can be obtained at a temperature of 280°C and the shear speed of 10<sup>2</sup>sec<sup>-1</sup>.  
 40

In the present invention, it is preferable to use amorphous polyolefin as the thermoplastic resin (b) of which Tg is at least 10°C higher than that of the thermoplastic polyester resin (a) such as a copolymer of norbornene/ethylene, a hydrogenate of ring opening polymer of dicyclopentadiene, random copolymers of ethylene/1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalenes (for example,  
 45 ethylene/2-ethyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, ethylene/2-methyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, ethylene/2-propyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, ethylene/2-hexyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, ethylene/2-stearyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene,  
 50 ethylene/2,3-dimethyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, ethylene/2-methyl-3-ethyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, ethylene/2-chloro-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, ethylene/2-bromo-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, ethylene/2-fluoro-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene, and ethylene/2,3-dichloro-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene) and copolymers of ethylene and at least one cyclic olefin selected from a group including cycloalkene and tricycloalkene (for example, bicyclo[2.2.1]hepto-2-ene,  
 55 6-methylbicyclo[2.2.1]hepto-2-ene,

*drawing of film creates fine irregularities*

5,6-dimethylbicyclo[2.2.1]hepto-2-ene,  
 1-methylbicyclo[2.2.1]hepto-2-ene,  
 6-ethylbicyclo[2.2.1]hepto-2-ene,  
 6-n-butylbicyclo[2.2.1]hepto-2-ene,  
 5 6-*i*-butylbicyclo[2.2.1]hepto-2-ene,  
 7-methylbicyclo[2.2.1]hepto-2-ene,  
 tricyclo[4.3.0.1<sup>2,5</sup>]-3-decene,  
 2-methyltricyclo[4.3.0.1<sup>2,5</sup>]-3-decene,  
 5-methyltricyclo[4.3.0.1<sup>2,5</sup>]-3-decene,  
 10 tricyclo[4.4.0.1<sup>2,5</sup>]-3-decene,  
 and 10-methyltricyclo[4.4.1.1<sup>2,5</sup>]-3-decene).

The typical amorphous polyolefin used in the present invention is copolymer of ethylene and the above-mentioned cyclic olefin. The content of the cyclic olefin component in the copolymer is generally more than 10 mol% and less than 60 mol%, and that of the ethylene component is generally more than 40 mol% and less than 90 mol%. Other copolymerizable unsaturated monomer component may be copolymerized with these two components, depending on necessity to such a degree that the object of the present invention can be achieved. The copolymerizable unsaturated monomers are, for example,  $\alpha$ -olefin in C<sub>3</sub> to C<sub>20</sub> such as propylene, 1-butene, 4-methylpentene-1, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, and 1-eicosene, cyclopentene, cyclohexene, 3-methylcyclohexene, cyclooctene, 1,4-hexadiene, 4-methyl-1-hexadiene, 5-methyl-1,4-hexadiene, 1,7-octadiene, dicyclopentadiene, 5-ethylidene-2-norbornene, 5-vinyl-2-norbornene, tetracyclodecene, 2-methyltetracyclodecene, and 2-ethyltetracyclodecene.

The copolymer may be made with a liquid phase polymerization method. The cyclic olefin copolymer can be obtained in accordance with a method disclosed in, for example, Japanese Patent Unexamined Prepublication No. 61-271308.

25 The amorphous polyolefin used in the present invention has T<sub>g</sub> which is at least 10°C higher, and preferably at least 20°C higher than T<sub>g</sub> of the thermoplastic polyester resin (a). If T<sub>g</sub> of the maleimide copolymeric resin is equal to or lower than that of the thermoplastic polyester resin, the drawing of the film made of their composition will cause plastic deformation of the maleimide copolymeric resin therein and fine irregularities on the surface of the film will not enough to be generated.

30 There is no restriction regarding to the molecular weight of the maleimide copolymeric resin used in the present invention, and such molecular weight is well enough to such a degree that melt viscosity of 500 to 50,000 poise can be obtained at a temperature of 280°C and the shear speed of 10<sup>2</sup>sec<sup>-1</sup>.

In a case where the surface-roughened film according to the present invention contains the particulate inert materials of inorganic compound (c), these particles are added into the film at any time. However, it is more effective to add at an optional timing during esterification process proceeds to the substantial polycondensation. It is also possible to directly incorporate these particulate inert materials of inorganic compound into the thermoplastic polyester resin (a) with no particulate inert materials of inorganic compound and mix them into a resin to be filmed. However, such method requires the particulate inert materials of inorganic compound (c) being well uniformly dispersed in the thermoplastic polyester resin (a).

40 In order to sufficiently disperse the particulate inert materials of inorganic compound (c) in the thermoplastic polyester resin (a), the particles should be grind into primary particles by using well-known devices such as an agitator, a sand mill, and a high-pressure dispersing machine. It is understood that a well-known polymerization method is preferably applied such that the particles are prevented from being aggregated or agglomerated with each other in the thermoplastic polyester resin (a) or that a dispersing agent should be added.

45 In addition, in order to improve adhesive properties to the thermoplastic polyester resin and to prevent occurrence of voids, the surface of the particulate inert materials of inorganic compound (c) may be previously treated. In this event, it is possible to use both chemical treatment such as treatment with silane coupling agent and a method applying to coating of acrylic compounds such as acrylic acid and acrylic ester and physical treatment such as corona (discharge) treatment.

50 Preferably, an average particle size of the particulate inert materials of inorganic compound (c) according to the present invention is within a range of 0.2 to 4.0  $\mu$ m, and more preferably, within a range of 1.0 to 3.5  $\mu$ m. The particulate inert materials of inorganic compound (c) having the average particle size of smaller than 0.2  $\mu$ m will not contribute to effectively improve the lubricity of the film, that is, there is no meaning to add such particles. On the other hand, the average particle size of larger than 4.0  $\mu$ m serves to degrade the film appearance into an unclear or opaque film because the appearance of the particles is highly related to its size. In addition, the refractive index of the particulate inert materials of inorganic compound (c) is preferably in the range of 1.40 to 1.68. If the refractive index is less than 1.40, which is significantly different from the refractive index of the polyester matrices, the transparency of the film will be decreased because of high reflection and

inert  
particles<sup>35</sup>

PS of  
particles<sup>50</sup>  
2-4  $\mu$ m

refraction of light at interfaces between dispersed particles and polyester resin matrices. The transparency of the film is improved as the refractive index approaches to 1.68, which is approximate to the refractive index of the drawn polyester film. The following minerals are generally but not limited to used as the particulate inert materials of inorganic compound: silica, calcium carbonate, alumina, talc, kaolin, zeolite, and alumino-silicate. The only important factor is the particle size.

The amount of the particulate inert materials of inorganic compound (c) used in this invention is preferably in the range of 0.0001 to 0.1 wt.%, and more preferably, 0.0001 to 0.05 wt.%, of the composition to be filmed.

When the particulate inert materials of inorganic compound (c) are contained in the surface-roughened film according to the present invention, it is preferable that the surface roughness S<sub>Ra</sub> of the surface-roughened film is in the range of 0.001 to 0.2  $\mu$ m and 0.007 to 0.07  $\mu$ m is more preferable, and that S<sub>Rz</sub> is within the range of 0.1 to 2.0  $\mu$ m, which is more preferable in the range of 0.1 to 0.5  $\mu$ m. The lubricity is insufficient with S<sub>Ra</sub> of smaller than 0.001  $\mu$ m and S<sub>Rz</sub> of smaller than 0.1  $\mu$ m, while the transparency of the film is insufficient with S<sub>Ra</sub> of larger than 0.2  $\mu$ m and S<sub>Rz</sub> of larger than 2.0  $\mu$ m.

The surface-roughened film according to the present invention may include, except for the particulate inert materials of inorganic compound, well-known organic slip agents, lubricants, antioxidants, anti-weathering agents, flame-retardants, antistatic agents, and some colorants to such a degree that the object of the present invention can be achieved.

The volume of the thermoplastic resin (b) used for the surface-roughened film according to this invention is in the range of 0.01 to 3.0 wt.% of the composition to be filmed, and preferably, in the range of 0.05 to 0.5 wt.%. This amount of thermoplastic resin (b) applied to the thermoplastic polyester resin (a) can be controlled in size of submicron (i.e. smaller than 1  $\mu$ m) due to shearing stress when being melt and mixed in a single or twin screw extruder.

With the surface-roughened film of the present invention, the effects of the invention can be equally obtained in a condition where one or more kinds of thermoplastic resins (b) are incorporated in the thermoplastic polyester resin (a). However, more advantageous effects can be obtained with the particulate inert materials of inorganic compound (c) in the range of 0.0001 to 0.1 wt.%, and more preferably, 0.0001 to 0.05 wt.%, co-existent with the thermoplastic resin (b).

A surface-roughened film of the present invention may be a single-layer film comprising a composition containing the thermoplastic polyester resin (a) and the thermoplastic resin (b) or the single-layer film comprising a composition containing the thermoplastic polyester resin (a), the thermoplastic resin (b) and the particulate inert materials of inorganic compound (c), and may be a laminated film laminated with other polymers. In case of the laminated film, the layer made of the composition is laminated with other polymers so that it forms surface layer of one or both side of the film. Such film is advantageous in that the transparency of the film is improved as well as economic. As the "other polymers", the thermoplastic polyester resins are generally applied such as PET, PBT, PEN, and PCT selected from the group including the thermoplastic polyester resin (a).

The surface-roughened film of the present invention is made by means of drawing an undrawn film comprising the composition of the thermoplastic polyester resin (a) and the thermoplastic resin (b) or the composition of the thermoplastic polyester resin (a), the thermoplastic resin (b), and the particulate inert materials of inorganic compound (c) or by means of drawing an undrawn laminate-film with the layer made of the composition and the other polymer layer at a temperature in the range of T<sub>g</sub> of the thermoplastic polyester resin (a) through T<sub>g</sub> of the thermoplastic resin (b). More particularly, the method used herein is applies to fuse and mix, in a single or twin screw extruder, the thermoplastic polyester resin (a) and the thermoplastic resin (b), or the thermoplastic polyester resin (a), the thermoplastic resin (b), and the particulate inert materials of inorganic compound (c) to cause fine dispersion of the thermoplastic resin (b) in the thermoplastic polyester resin (a). The resulting composition alone or with other polymers, if being laminated, is melt extruded into a film by using a T-die or a circular die to cool with a casting roll or cooling liquid/air. The resulting undrawn film has relatively smooth surfaces, which becomes irregular by being drawn. In this event, it is required that the drawing temperature is in the range of T<sub>g</sub> of the thermoplastic polyester resin (a) through T<sub>g</sub> of the thermoplastic resin (b). The drawing is not effectively made at a temperature lower than T<sub>g</sub> of the thermoplastic polyester resin (a), while desired surface irregularities is not readily caused at a temperature higher than T<sub>g</sub> of the thermoplastic resin (b). A draw ratio is a factor of one and half or more in both longitudinal and transversal directions (i.e. machine and cross directions) for uniaxial drawing. Biaxial drawing is desirable where the better film can be obtained. In this event, it is desirable to draw the film by not less than a factor of one and half, and preferably, by not less than a factor of three in both longitudinal and transversal directions.

Any one of the drawing method can be available such as the uniaxial drawing, sequential biaxial drawing, and simultaneous biaxial drawing. In addition, various types of drawing machines can be used such as a twin roll uniaxial drawing machine, a tenter transversal drawing machine, simultaneous biaxial drawing machine, and a tubular simultaneous biaxial drawing machine.

amt of particles  
0.0001-0.1 wt%

additives

amt of (b)  
0-3%

single layer  
or multilayer

other resin  
same as polymer (a)

drawing controls irregularity

drawing step

Biaxially drawing is preferred



When using only the particular inert materials of inorganic compound (c) as the anti-blocking agents, a haze (Hz) of a well-transparent film is in the range of 0.3 to 2.5 %. However, the film of the type described tends to cause protuberances on a rolled film upon rolling up the film due to a static friction coefficient by line press method of more than 2.5, which may be a defect that the well-rolled film is not readily obtained.

In the surface-roughened film according to the present invention, Hz of the film thickness converted value is, as a 100  $\mu\text{m}$  converted value, 0.3 to 2.5 %, the static friction coefficient by line press method ( $\mu\text{s-2}$ ) under loading of 1,000 g/cm is less than 2.4, and a gloss rate (G%) is 180 to 250 %.

According to the surface-roughened film and the method for fabricating such film of the present invention, it can be realized to manufacture the surface-roughened film with addition of synthetic organic resins, which is difficult by using a conventional methods. Such film has considerably variable in various industries in its working properties, mechanical properties, lubricity and transparency of the resultant film.

The surface-roughened film provided in accordance with the present invention is useful for a photoengraving material, a label, a wrapping film, a magnetic recording film, and a clear film or other products.

Detailed description will be made with some examples.

(Thermoplastic polyester resin)

A thermoplastic polyester resin (a) used in this embodiment is given in the following Table 1.

TABLE 1

| Thermoplastic polyester resin | Intrinsic Viscosity<br>[ $\eta$ ] | Critical Surface Tension<br>(dyne/cm) | Tg<br>(°C) |
|-------------------------------|-----------------------------------|---------------------------------------|------------|
|-------------------------------|-----------------------------------|---------------------------------------|------------|

|     |                            |      |    |     |
|-----|----------------------------|------|----|-----|
| A-1 | Polyethylene terephthalate | 0.78 | 41 | 70  |
| A-2 | Polyethylene naphthalate   | 0.70 | 38 | 120 |

(Synthesis of amorphous nylon)

Prepared in a reactor was a raw material of 10 kg containing 1,3-benzenedicarboxylic acid (isophthalic acid) of 45 mol%, 1,4-benzenedicarboxylic acid (terephthalic acid) of 5 mol%, hexamethylene diamine of 45 mol%, bis(4-amino-3-methylcyclohexyl) methane of 5 mol% and acetic acid of 0.015 mol% with pure water of 8 kg to purge the air within the reactor by using nitrogen. The temperature was raised up to 90 °C to react for about five hours, then the reaction temperature was gradually raised up to 280°C for over ten hours under pressure (18 bar) agitating in the reactor. The pressure was decreased to atmospheric pressure to polymerize for six hours at the same temperature. After the reaction, nylons were taken from the reactor to be cut into pellets. The relative viscosity of this nylon (B-1), measured at a level of 1g/dl in m-cresol at a temperature of 20°C, was 1.50 and Tg was 150°C.

The other amorphous nylons were polymerized in the same manner. The result is shown in Table 2.

TABLE 2

|     | 1    | 2  | 3  | 4 | 5 | 6 | 7    | 8  | Melt<br>Viscosity (poise) | Tg<br>(°C) |
|-----|------|----|----|---|---|---|------|----|---------------------------|------------|
| B-1 | 45   | 5  | 45 | 5 | - | - | -    | -  | 2600                      | 150        |
| B-2 | 15.5 | 32 | 29 | - | - | 5 | 13.5 | -  | 2500                      | 167        |
| B-3 | 50   | -  | -  | - | - | - | -    | 50 | 5000                      | 177        |
| B-4 | 45   | -  | 45 | 5 | 5 | - | -    | -  | 2000                      | 118        |
| B-5 | 45   | 5  | 45 | 5 | - | - | -    | -  | 450                       | 150        |

1...isophthalic acid

2...terephthalic acid

3...hexamethylenediamine

4...bis(4-amino-3-methylcyclohexyl)methane

5...sebacic acid

6...caprolactam

7...3-aminomethyl-3,5,5-trimethylcyclohexylamine

8...methoxylenediamine

(Synthesis of maleimide copolymeric resin)

Approximately 100 parts of styrene, approximately 67 parts of maleic anhydride, 0.2 parts of benzoyl peroxide, and 300 parts of methyl ethyl ketone (MEK) were reacted in nitrogen atmosphere for 10 hours at a temperature of 80°C. The resultant polymer was added with 1.2 parts of triethylamine and 46.2 parts of aniline and reacted for 6 hours at a temperature of 130 °C to obtain the maleimide copolymeric resin (C-3). Other maleimide polymeric resins were made in the same manner. The result is given in Table 3.

TABLE 3

| Copolymer | Monomer Composition (mol%) |                   |                               |                 |  | Tg (°C) | Melt Viscosity (poise) |
|-----------|----------------------------|-------------------|-------------------------------|-----------------|--|---------|------------------------|
|           | Aromatic vinyl monomer     | maleimide monomer | unsaturated dicarboxylic acid | Other Monomers* |  |         |                        |
| C-1       | ST 30                      | NPM 50            |                               | MMA 20          |  | 200     | 11000                  |
| 2         | ST 50                      | NPM 5             | MAH 45                        |                 |  | 203     | 12000                  |
| 3         | ST 60                      | NPM 40            |                               |                 |  | 197     | 9000                   |
| 4         | ST 50                      | NPM 30            | MAH 20                        |                 |  | 203     | 12000                  |
| 5         | ST 40                      | NPM 60            |                               |                 |  | -       | -                      |
| 6         | ST 90                      | NPM 10            |                               |                 |  | 120     | 2500                   |
| 7         | ST 30                      | NPM 10            | MAH 60                        |                 |  | -       | -                      |
| 8         | ST 10                      | NPM 30            |                               | MMA 60          |  | -       | -                      |
| 9         | ST 95                      |                   | MAH 5                         |                 |  | 90      | 2300                   |
| 10        | VT 50                      | NPM 50            |                               |                 |  | 203     | 12000                  |
| 11        | ST 50                      | NTM 50            |                               |                 |  | 203     | 12000                  |
| 12        | ST 60                      | NPM 40            |                               |                 |  | 198     | 55000                  |

ST :styrene

VT :vinyltoluene

NPM:N-phenylmaleimide

NTM:N-tolylmaleimide

MAH:maleic anhydride

MMA:methyl methacrylate

\* = copolymerizable monomers

## (Synthesis of amorphous polyolefin)

To 6-ethylbicyclo[2.2.1]hepto-2-ene of 60g and one liter of toluene, a vanadium compound of  $\text{VO}(\text{OC}_2\text{H}_5)_2\text{Cl}_2$  and ethylaluminum sesquichloride were added with the ratio of 1 mmol per liter and 4 mmol per liter, respectively, in the prepared composition to be reacted. 40 liters of ethylene per hour and 80 liters of nitrogen per hour was provided to the reactor to react the composition therein. The copolymerization were continuously conducted at a temperature of 10°C. Subsequently, a little amount of methanol was added to inhibit polymerization. A ring olefin copolymer (D) was obtained by precipitating the aimed amorphous polyolefin using a large amount of acetone/methanol. The resultant copolymer and its properties are shown in Table 4 below.

TABLE 4

| Copolymer | Cyclic olefin                        | Ethylene contents in<br>Cyclic olefin<br>copolymer (mol%) | Melt<br>Viscosity °C<br>(poise) | Tg  |
|-----------|--------------------------------------|---|---------------------------------|-----|
| D         | 6-ethylbicyclo<br>[2.2.1]hepto-2-ene | 62  | 2500                            | 100 |

Measuring devices and methods used in this embodiment are as follows:

## (Dispersed particle diameter)

The dispersed particle diameter was determined from an electron micrograph of sample rupture cross-section by using a scanning electron microscope JSM-15, obtained from the JEOL Ltd.

## (Surface roughness)

It was determined in accordance with the method defined in JIS B 0601 (1976) using a surface roughness tester obtained from the KOSAKA Co. Ltd. with a stylus of 2  $\mu\text{m}$ R in radius, 10mg in pressure, and at a 50,000 height magnification.

## (Haze, Hz)

It was determined in accordance with ASTM D1003-61 using a Haze meter available from the TOKYO DENSHOKU Co. Ltd.

## (Friction coefficient)

Using a friction meter sold by the Shinto Kagaku Ltd. under the name of HEIDON-14S/DR, a static friction coefficient by plane press method ( $\mu\text{s}-1$ ) was measured with a flat shape indenter of  $3 \times 3 \text{ cm}^2$  and the static friction coefficient by line press method ( $\mu\text{s}-2$ ) was measured with a straight shape indenter of 15mm in radius and 10mm in length. They were measured under the condition where loading was 1kg and the moving speed of 150 mm/min.

## (Refraction Index)

Measured in film of 250  $\mu\text{m}$  in thickness by using an Abbe's refractometer IT sold by the ATAGO Ltd.

(Critical Surface Tension)

Measured at a temperature of 20°C and a relative humidity (RH) of 50% using an automatic contact angle meter CA-Z by the Kyowa Interface Science Co. Ltd.

(G%)

The Gloss rate at an angle of incidence to the film of 20 degree was measured using a gloss meter GM-30 sold by the Murakami Color research Laboratory Ltd.

(Melt Viscosity)

It was measured using a flow tester CFT-500 sold by Shimadzu Corp. with an orifice of 0.5 mm  $\Phi$  in diameter and 2mm in height at a temperature of 280°C.

(Evaluation for protuberances: the number of protuberances on the surface of 1,000m wind roll having a width of 1m)

Meaning of the symbols are:

- X: protuberances were found under the condition that contact pressure of 10kg/m and tension of 10kg/m on film slitting;
- : no protuberances were found under the condition that contact pressure of 10kg/m and tension of 10kg/m on film slitting and less than five protuberances were found under the condition that contact pressure of 20kg/m and tension of 20kg/m; and
- ⊙: no protuberances were found under both conditions that contact pressure of 10kg/m and tension of 10kg/m and that contact pressure of 20kg/m and tension of 20kg/m.

(Examples 1 to 3)

The thermoplastic polyester resin (A-1) of 95 wt.% and amorphous nylons (B-1 to B-3) of 5wt.% were melt and blend into pellets at a temperature of 280°C using a biaxial kneading extruder. Thereafter, the resultant pellets and the thermoplastic (A-1) were formulated under the additive ratio of the amorphous nylon set forth below in Table 5 by means of two-kinds-three-layer T-die using two extruders of 50mm  $\Phi$  and 65mm $\Phi$ . A three-layer laminated polyester film having thickness of 700  $\mu$ m were obtained, where the mixed pellets were formed as outer layers (56  $\mu$ m x 2) and PET (A-1) was formed as an inner layer (588  $\mu$ m). In order to measure the diameter of particles of the thermoplastic resin dispersed in the undrawn film, the size were determined from an electron micrograph of the rupture cross-section of a sample obtained by exposing the undrawn film to frost-rupture in liquid nitrogen along takeup direction or machine direction (MD) of the film. The undrawn film was then drawn in longitudinal direction (machine direction) by a factor of three and half using a longitudinal drawing roll at a temperature of 90°C and succeedingly drawn in transversal direction (cross-direction) by a factor of four using a transversal tenter drawing machine at a raised temperature of 120°C.

Formulations, properties of the thermoplastic resin (amorphous nylon), dispersed particle diameters of the thermoplastic resin and properties of the drawn films are shown in Tables 5 to 8. It is clear from these tables that the film fabricated in accordance with the present invention exhibits superior surface roughness, haze, static friction coefficient by line press method, and protuberance free surface when compared to controls, with respect to contents, the critical surface tension and the melt viscosity defined by the present invention, and to a preferred specific condition of the refractive index and the dispersed particle diameter.

(Control 1)

The thermoplastic polyester resin prepared with A-2 and the thermoplastic resin prepared with B-4 were pelletized after being kneaded in the same formulation as Examples 1 to 3. Thereafter, the undrawn film was obtained in the same manner as described in Examples 1 to 3 using the thermoplastic polyester resin A-2 for the inner layer. The film was drawn under the same condition as described in Examples 1 to 3 except that the drawing temperature for the longitudinal roll was 130°C and that for the transversal tenter extruder was 150°C. The properties of the drawn film are shown in Table 7. It can be seen from Table 7 that thermoplastic resins having Tg of lower than that of the thermoplastic polyester resin exhibited high transparency whereas the lubricity was not preferred and some protuberances were found.

(Control 2)

The drawn film was prepared in the same manner as described in Examples 1 to 3 except that a nylon6 (Tg of 45 °C) was used as the thermoplastic resin.

Like the foregoing control 1, thermoplastic resins having Tg of lower than that of the thermoplastic polyester was used resulting the high transparency, whereas the lubricity was not preferred and some protuberances were found.

(Controls 3 to 5)

The drawn film was prepared in the same manner as described in Examples 1 to 3 with the thermoplastic polyester resin and the thermoplastic resin as set forth in Table 5 in accordance with the ratio as set forth in Table 5. The result is shown in Table 7. It was found that the resultant film inevitably exhibited excessive haze under the condition that the contents and the melt viscosity of the thermoplastic resin was over the range defined by the present invention, while only the film having protuberances on its surface was obtained even when the haze was lower than 2.5%.

(Controls 6 to 8)

Silica SY-150 sold by Nippon Shokubai Co.Ltd. was added to the thermoplastic polyester resin (A) on its polymerization and a silica master pellet was substituted for the thermoplastic resin (b) in Examples 1 to 3 to obtain the drawn film in the same manner as described in Examples 1 to 3. The processing conditions are given in Table 5 and the results in Table 7.

It was found from these controls that the film of high quality was not obtained because protuberances were generated on the surface of the film roll or the haze were higher than 2.5 %.

(Examples 4 to 10)

The drawn film was fabricated in the same manner as described in Examples 1 to 3 except that the silica set forth in Tables 5 and 6 was added at a concentration set forth in Tables 5 and 6 with a preformed master pellet like the foregoing Example 2. The results are shown in Tables 7 and 8. It was found that advantageous effects and superior results were obtained by means of coexisting the thermoplastic resin and the particulate inert materials of inorganic compound at the volume defined by the present invention in the thermoplastic polyester resin.

(Control 9)

The same processing was made as Example 4 besides that the silica having the larger particle diameter than that defined by the present invention as shown in Tables 6 and 8. As a result, it was found that the film exhibited lower transparency as well as good lubricity when being coexisted with the thermoplastic resin (b) defined by the present invention.

(Control 10)

The same processing was made as Example 4 besides that the thermoplastic resin having the Tg as shown in Tables 6 and 8. As a result, it was found that the film exhibited disadvantageous lubricity as well as high transparency of the film and some protuberances were generated when being coexisted with the silica defined by the present invention.

(Examples 11 to 14)

*Maleimide as B*  
Tables 6 and 8 shows that the transparency and the lubricity of the film was not affected by using the maleimide copolymeric resin and the amorphous polyolefin as the thermoplastic resin (b).

(Control 11)

The film was prepared in the same manner as Example 4 besides that the drawing was made only with the longitudinal drawing roll for 1.4 times. Some protuberances were found on the film surface.

(Control 12)

The same processing was made as Example 1 besides that the maleimide copolymeric resin (C-12) having the melt viscosity greater than that defined by the present invention was used as the thermoplastic resin (b).  
5 As a result, it was found that the transparency of the film was degraded with the particles of larger particle diameter.

(Control 13)

10 The same processing was made as Example 4 besides that the silica of 0.1  $\mu\text{m}$  in diameter. As a result, it was found that the properties of the film was similar to that in Example 2 with the particulate inert materials of inorganic compound having the diameter of smaller than the range defined by the present invention, only to exhibit it is not effective to add the particulate inert materials of inorganic compound.

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Table 5

| Thermoplastic Polyester Resin (a) |              | Thermoplastic Resin (b) |                      |                                  |                                    | Inorganic Inert Particles |                        |             |                      |                        |                  |
|-----------------------------------|--------------|-------------------------|----------------------|----------------------------------|------------------------------------|---------------------------|------------------------|-------------|----------------------|------------------------|------------------|
|                                   | Formulations | Tg (°C)                 | Addition Rate (wt.%) | Dispersed Particle Diameter (μm) | Critical Surface Tension (dyne/cm) | Refractive Index          | Melt Viscosity (poise) | Formulation | Addition Rate (wt.%) | Particle Diameter (μm) | Refractive Index |
|                                   |              |                         |                      |                                  |                                    |                           |                        |             |                      |                        |                  |
| PET D1690                         |              |                         |                      |                                  |                                    |                           |                        |             |                      |                        |                  |
| Example 1                         | A-1          | 150                     | 0.1                  | 0.21                             | 46                                 | 1.49                      | 2600                   | -           | -                    | -                      | -                |
| Example 2                         | A-1          | 167                     | 0.1                  | 0.25                             | 44                                 | 1.48                      | 4000                   | -           | -                    | -                      | -                |
| Example 3                         | A-1          | 177                     | 0.1                  | 0.20                             | 44                                 | 1.62                      | 5000                   | -           | -                    | -                      | -                |
| Control 1                         |              |                         |                      |                                  |                                    |                           |                        |             |                      |                        |                  |
| Control 1                         | A-2          | 118                     | 0.1                  | 0.18                             | 46                                 | 1.49                      | 2000                   | -           | -                    | -                      | -                |
| Control 2                         | A-1          | NYLON6                  | 45                   | 0.1                              | 44                                 | 1.53                      | 2000                   | -           | -                    | -                      | -                |
| Control 3                         | A-1          | 167                     | 0.005                | 0.17                             | 44                                 | 1.48                      | 4000                   | -           | -                    | -                      | -                |
| Control 4                         | A-1          | 167                     | 4.0                  | 0.85                             | 44                                 | 1.48                      | 4000                   | -           | -                    | -                      | -                |
| Control 5                         | A-1          | 150                     | 0.1                  | 0.05                             | 46                                 | 1.49                      | 400                    | -           | -                    | -                      | -                |
| Control 6                         | A-1          | -                       | -                    | -                                | -                                  | -                         | -                      | silica      | 0.0045               | 2.0                    | 1.44             |
| Control 7                         | A-1          | -                       | -                    | -                                | -                                  | -                         | -                      | silica      | 0.050                | 2.0                    | 1.44             |
| Control 8                         | A-1          | -                       | -                    | -                                | -                                  | -                         | -                      | silica      | 0.0001               | 2.0                    | 1.44             |
| Example 4                         |              |                         |                      |                                  |                                    |                           |                        |             |                      |                        |                  |
| Example 4                         | A-1          | 167                     | 0.1                  | 0.25                             | 44                                 | 1.48                      | 4000                   | silica      | 0.0045               | 2.0                    | 1.44             |
| Example 5                         | A-1          | 167                     | 0.1                  | 0.25                             | 44                                 | 1.48                      | 4000                   | silica      | 0.030                | 2.0                    | 1.44             |
| Example 6                         | A-1          | 167                     | 0.1                  | 0.25                             | 44                                 | 1.48                      | 4000                   | silica      | 0.0005               | 2.0                    | 1.44             |



Table 6

| Thermoplastic Polyester Resin (a) |     | Thermoplastic Resin (b) |     |         |                      |                                  | Inorganic Inert Particles          |                  |                        |             |                      |                        |                  |
|-----------------------------------|-----|-------------------------|-----|---------|----------------------|----------------------------------|------------------------------------|------------------|------------------------|-------------|----------------------|------------------------|------------------|
|                                   |     | Formulations            |     | Tg (°C) | Addition Rate (wt.%) | Dispersed Particle Diameter (μm) | Critical Surface Tension (dyne/cm) | Refractive Index | Melt Viscosity (poise) | Formulation | Addition Rate (wt.%) | Particle Diameter (μm) | Refractive Index |
| Example 7                         | A-1 | B-2                     | 167 | 2.5     | 0.41                 | 44                               |                                    | 1.48             | 4000                   | silica      | 0.0001               | 2.0                    | 1.44             |
| Example 8                         | A-1 | B-2                     | 167 | 0.01    | 0.20                 | 44                               |                                    | 1.48             | 4000                   | silica      | 0.050                | 2.0                    | 1.44             |
| Control 9                         | A-1 | B-2                     | 167 | 0.1     | 0.25                 | 44                               |                                    | 1.48             | 4000                   | silica      | 0.0045               | 5.0                    | 1.44             |
| Example 9                         | A-1 | B-2                     | 167 | 0.01    | 0.20                 | 44                               |                                    | 1.48             | 4000                   | silica      | 0.050                | 2.0                    | 1.68             |
| Example 10                        | A-1 | B-3                     | 177 | 0.1     | 0.20                 | 44                               |                                    | 1.62             | 5000                   | silica      | 0.0045               | 2.0                    | 1.44             |
| Control 10                        | A-1 | NYLON6                  | 45  | 0.1     | 0.18                 | 44                               |                                    | 1.53             | 2000                   | silica      | 0.0045               | 2.0                    | 1.44             |
| <i>Material Example</i>           |     |                         |     |         |                      |                                  |                                    |                  |                        |             |                      |                        |                  |
| Example 11                        | A-1 | C-3                     | 197 | 0.1     | 0.41                 | 40                               |                                    | 1.59             | 9000                   | -           | -                    | -                      | -                |
| Example 12                        | A-1 | C-3                     | 197 | 0.1     | 0.41                 | 40                               |                                    | 1.59             | 9000                   | silica      | 0.0045               | 2.0                    | 1.44             |
| Example 13                        | A-1 | D                       | 100 | 0.1     | 0.38                 | 30                               |                                    | 1.51             | 2500                   | -           | -                    | -                      | -                |
| Example 14                        | A-1 | D                       | 100 | 0.1     | 0.38                 | 30                               |                                    | 1.51             | 2500                   | silica      | 0.0045               | 2.0                    | 1.44             |
| Control 11                        | A-1 | B-2                     | 167 | 0.1     | 0.25                 | 44                               |                                    | 1.48             | 4000                   | silica      | 0.0045               | 2.0                    | 1.44             |
| Control 12                        | A-1 | C-12                    | 198 | 0.1     | 1.21                 | 40                               |                                    | 1.59             | 55000                  | -           | -                    | -                      | -                |
| Control 13                        | A-1 | B-2                     | 167 | 0.1     | 0.25                 | 44                               |                                    | 1.48             | 4000                   | silica      | 0.0045               | 0.1                    | 1.44             |

Table 7

| Film Surface Roughness |            |         | Film Properties |        |      | μ s -2<br>Protuberances |   |
|------------------------|------------|---------|-----------------|--------|------|-------------------------|---|
| SRa<br>μ m             | SRz<br>μ m | Hz<br>% | G%<br>%         | μ s -1 |      |                         |   |
| Example 1              | 0.0084     | 0.110   | 0.8             | 245    | 0.48 | 0.56                    | ○ |
| Example 2              | 0.0072     | 0.132   | 0.7             | 244    | 0.47 | 0.55                    | ○ |
| Example 3              | 0.0066     | 0.138   | 0.5             | 240    | 0.45 | 0.52                    | ○ |
| Control 1              | 0.0045     | 0.009   | 0.9             | 253    | 1.20 | 2.76                    | × |
| Control 2              | 0.0038     | 0.009   | 1.0             | 254    | 1.25 | 3.52                    | × |
| Control 3              | 0.0039     | 0.080   | 0.9             | 251    | 1.22 | 3.31                    | × |
| Control 4              | 0.07       | 1.80    | 6.9             | 145    | 0.41 | 0.49                    | ○ |
| Control 5              | 0.0050     | 0.008   | 1.8             | 249    | 0.68 | 2.41                    | × |
| Control 6              | 0.0092     | 0.39    | 0.5             | 253    | 1.09 | 2.83                    | × |
| Control 7              | 0.0045     | 2.1     | 4.8             | 169    | 0.41 | 0.51                    | ○ |
| Control 8              | 0.0013     | 0.148   | 0.3             | 260    | 1.25 | 3.52                    | × |
| Example 4              | 0.0120     | 0.33    | 0.9             | 235    | 0.31 | 0.48                    | ⊙ |
| Example 5              | 0.0138     | 0.38    | 1.9             | 221    | 0.25 | 0.47                    | ⊙ |
| Example 6              | 0.0074     | 0.18    | 0.8             | 243    | 0.35 | 0.48                    | ⊙ |

Table 8

| Film Surface Roughness |                |         |         | Film Properties |      |   | $\mu$ s -2<br>Protuberances |
|------------------------|----------------|---------|---------|-----------------|------|---|-----------------------------|
| SRa<br>$\mu$ m         | SRz<br>$\mu$ m | Hz<br>% | G%<br>% | $\mu$ s -1      |      |   |                             |
| Example 7              | 0.019          | 0.42    | 218     | 0.24            | 0.45 | ⊙ |                             |
| Example 8              | 0.0081         | 0.38    | 220     | 0.23            | 0.46 | ⊙ |                             |
| Control 9              | 0.062          | 2.30    | 201     | 0.29            | 0.46 | ⊙ |                             |
| Example 9              | 0.0080         | 0.42    | 228     | 0.23            | 0.45 | ⊙ |                             |
| Example 10             | 0.0071         | 0.43    | 236     | 0.27            | 0.42 | ⊙ |                             |
| Control 10             | 0.0037         | 0.32    | 234     | 0.87            | 2.55 | × |                             |
| Example 11             | 0.0073         | 0.14    | 241     | 0.57            | 0.56 | ○ |                             |
| Example 12             | 0.0080         | 0.37    | 230     | 0.43            | 0.52 | ⊙ |                             |
| Example 13             | 0.0069         | 0.12    | 248     | 0.56            | 0.54 | ○ |                             |
| Example 14             | 0.0078         | 0.35    | 220     | 0.42            | 0.44 | ⊙ |                             |
| Control 11             | 0.0031         | 0.075   | 255     | 1.23            | 3.52 | × |                             |
| Control 12             | 0.064          | 2.31    | 198     | 0.31            | 0.49 | ○ |                             |
| Control 13             | 0.0071         | 0.132   | 244     | 0.46            | 0.55 | ○ |                             |

(Examples 15 to 17)

PET (A-1) and the amorphous nylon (B-1) were melt and mixed into pellets using a biaxial kneading extruder at a temperature of 280°C in a different mixture ratio.

Subsequently, these pellets were melt at the same temperature of 280°C using an extruder of 50 mm  $\Phi$  and extruded from a T-die into the film having a thickness of approximately 500  $\mu\text{m}$ . The resultant undrawn film was uniaxially drawn by a factor of three using a two-roll uniaxial drawing machine at a temperature of 90°C. Film properties are shown in Table 9, where it can be found that these drawn films are superior in the mechanical properties, lubricity and transparency.

TABLE 9

| Case No.   | Weight ratio of<br>(A-1):(B-1) | Mechanical<br>Properties | Hz<br>(%) | $\mu\text{s-1}$ | $\mu\text{s-2}$ |
|------------|--------------------------------|--------------------------|-----------|-----------------|-----------------|
| Example 15 | 99.9:0.1                       | well                     | 1.0       | 0.57            | 0.63            |
| Example 16 | 99.0:1.0                       | well                     | 1.5       | 0.49            | 0.56            |
| Example 17 | 97.0:3.0                       | well                     | 2.5       | 0.40            | 0.50            |

(Example 18)

The undrawn film like Example 17 was simultaneously drawn in both longitudinal and transversal directions by a factor of 3.3 at a temperature of 100°C, and was heatset thereafter at a raised temperature of 230°C. The properties of the resultant drawn film were well as shown in Table 10. In this event, the measuring direction is the longitudinal direction of the film.

TABLE 10

|                                     | Unit               | Value |     |
|-------------------------------------|--------------------|-------|-----|
|                                     |                    | L*    | T*  |
| Breaking Strength                   | kg/mm <sup>2</sup> | 21    | 20  |
| Breaking Extension                  | %                  | 135   | 120 |
| Heat Shrinkage<br>(160°C x 15 min.) | %                  | 1.4   | 0.1 |
| $\mu S-2$                           |                    | 0.53  |     |

\* L=longitudinal direction    T=transversal direction

(Example 19)

With a co-extruding film fabricating device having three extruders of 40 mm  $\Phi$ , an undrawn laminated film was fabricated such that the polyethylene terephthalate layer of 300  $\mu$ m was laid between 100  $\mu$ m layers of mixed resin of which composition was identical to that of Example 16. This undrawn film was longitudinally drawn by a factor of 3.3 using a roll-type longitudinal drawing machine at a temperature of 90°C. Subsequently, it was transversally drawn by a factor of 3.4 using a tenter drawing machine at a raised temperature of 100°C to immediately carry out heatsetting.

The surface roughness of the drawn film was relatively high as shown in Table 11 and the lubricity thereof was adequate. In this event, the measuring direction was the longitudinal direction of the film.

TABLE 11

|                                     | Unit               | Value |      |
|-------------------------------------|--------------------|-------|------|
|                                     |                    | L*    | T*   |
| Breaking Strength                   | kg/mm <sup>2</sup> | 24    | 23   |
| Breaking Extension                  | %                  | 120   | 115  |
| Heat Shrinkage<br>(160°C x 15 min.) | %                  | 1.0   | 0.1  |
| $\mu$ s-2                           |                    |       | 0.78 |

\* L=longitudinal direction T=transversal direction

(Example 20, Controls 14 and 15)

An uniaxial drawing test was conducted using the amorphous nylon (B-4) and (B-1) and PEN (A-2) in a similar manner as the Examples 15 to 17 under the composition and temperature set forth in Table 12. As clearly shown from Table 12, T<sub>g</sub> and the drawing temperature of the amorphous nylon plays an important role to roughen the film surface.

TABLE 12

| Case No.   | Weight ratio of<br>(A-2):(B-1):(B-4) | Drawing<br>Temperature (°C) | $\mu$ s-1 | $\mu$ s-2 |
|------------|--------------------------------------|-----------------------------|-----------|-----------|
| Example 20 | 99 : 1.0 : 0                         | 140                         | 0.52      | 0.60      |
| Control 14 | 99 : 1.0 : 0                         | 160                         | 1.2       | 3.31      |
| Control 15 | 99 : 0 : 1.0                         | 140                         | 1.2       | 3.38      |

(Examples 21 to 23)

PET (A-1) and the maleimide copolymeric resin (C-3) were melt and mixed into pellets using a biaxial kneading extruder at a temperature of 280°C in a different mixture ratio.

Subsequently, these pellets were melt at the same temperature of 280°C using an extruder of 50mm  $\Phi$  and extruded from a T-die into the film having a thickness of approximately 500  $\mu$ m. The resultant undrawn film was uniaxially drawn by a factor of three using a two-roll uniaxial drawing machine at a temperature of

90°C. Compositions are shown in Table 13, where it can be found that these drawn films were superior in the mechanical properties and transparency. In addition, no measured static friction coefficient were larger than 1.0. This means that the films have considerably high lubricity.

TABLE 13

| Case No.   | Weight ratio of<br>(A-1):(C-3) | Tensile<br>Strength<br>(Kg/mm <sup>2</sup> ) | Hz<br>(%) | $\mu$ s-1 | $\mu$ s-2 |
|------------|--------------------------------|--|-----------|-----------|-----------|
| Example 21 | 99.9:0.1                       | 21   | 1.0       | 0.57      | 0.56      |
| Example 22 | 99.0:1.0                       | 22   | 1.5       | 0.49      | 0.48      |
| Example 23 | 97.0:3.0                       | 20   | 3.1       | 0.40      | 0.41      |

(Measuring direction : The longitudinal direction of the film)

(Example 24)

The undrawn film like Example 23 was simultaneously drawn in both longitudinal and transversal directions by a factor of 3.3 at a temperature of 100°C, and was heatset thereafter at a raised temperature of 230°C. The properties of the resultant drawn film were well as shown in Table 14.

TABLE 14

|                    | Unit               | Value |      |
|--------------------|--------------------|-------|------|
|                    |                    | L*    | T*   |
| Tensile Strength   | kg/mm <sup>2</sup> | 22    | 21   |
| Breaking Extension | %                  | 120   | 115  |
| Heat Shrinkage     | %                  | 1.2   | 0.1  |
| (160°C x 15 min.)  |                    |       |      |
| $\mu$ s-2          |                    |       | 0.52 |

\* L=longitudinal direction T=transversal direction

(Examples 25 to 29 and Controls 16 to 19)

PET (A-1) and the maleimide copolymeric resin at a ratio of 99.9:0.1 were fabricated into the undrawn film in accordance with the method as described in Examples 21 to 23, and also fabricated into the drawn film in accordance with the method as described in Example 24 to clarify the effects of each maleimide copolymeric resins. The results are shown in Table 15. From Table 15, it was found the optimum drawability and properties of films were achieved with the maleimide copolymeric resin having following composition: maleimide monomer of 5 to 50 mol%, unsaturated dicarboxylic anhydride monomer groups of 0 to 50 mol%, aromatic vinyl monomer groups of 30 to 90 mol%, and other copolymerizable monomer groups of 0 to 50 mol %, and any other concentration more or less adversely affected to degrading of drawability and performance of the film.

TABLE 15

| Case No.   | Maleimide Copolymer | Drawability | Tensile Strength<br>(Kg/mm <sup>2</sup> ) | Hz (%) | $\mu$ s-1 | $\mu$ s-2 |
|------------|---------------------|-------------|---|--------|-----------|-----------|
| Example 25 | C-1                 | well        | 23  | 1.3    | 0.49      | 0.56      |
| Example 26 | C-2                 | well        | 20  | 1.2    | 0.48      | 0.56      |
| Example 27 | C-4                 | well        | 23  | 1.2    | 0.50      | 0.57      |
| Example 28 | C-10                | well        | 22  | 1.0    | 0.48      | 0.56      |
| Example 29 | C-11                | well        | 24  | 1.0    | 0.47      | 0.55      |
| Control 16 | C-5                 | broken      | -   | -      | -         | -         |
| Control 17 | C-7                 | broken      | -   | -      | -         | -         |
| Control 18 | C-8                 | broken      | -   | -      | -         | -         |
| Control 19 | C-9                 | well        | 9   | 1.5    | 2.10      | 6.76      |

(Example 30)

With a co-extruding film fabricating device having three extruders of 40 mm  $\Phi$ , an undrawn laminated film was fabricated such that the polyethylene terephthalate layer of 300  $\mu$ m was laid between 100  $\mu$ m layers of mixed resin of which composition was identical to that of Example 22. This undrawn film was longitudinally drawn by a factor of 3.3 using a roll-type longitudinal drawing machine at a temperature of 90°C. Subsequently, it was transversally drawn by a factor of 3.4 using a tenter drawing machine at a raised temperature of 100°C to immediately carry out heatsetting.

The surface roughness of the drawn film was relatively high as shown in Table 16 and the lubricity thereof was adequate. Further, the mechanical properties are also superior as shown in Table 16.



TABLE 16

|                    | Unit               | Value |      |
|--------------------|--------------------|-------|------|
|                    |                    | L*    | T*   |
| Tensile Strength   | kg/mm <sup>2</sup> | 24    | 22   |
| Breaking Extension | %                  | 130   | 125  |
| Heat Shrinkage     | %                  | 1.0   | 0.1  |
| (160°C x 15 min.)  |                    |       |      |
| $\mu s-2$          |                    |       | 0.53 |

\* L=longitudinal direction    T=transversal direction

(Example 31 and Controls 20 and 21)

An uniaxial drawing test was conducted using the maleimide copolymeric resin (C-3) and (C-6) and PEN (A-2) in a similar manner as the Examples 21 to 23 under the composition and temperature set forth in Table 17. As clearly shown from Table 17, Tg and the drawing temperature of the amorphous nylon plays an important role to roughen the film surface.

TABLE 17

| Case No.   | Weight ratio of<br>(A-2):(C-3):(C-6) | Drawing<br>Temperature<br>(°C) | $\mu s-1$ | $\mu s-2$ |
|------------|--------------------------------------|--------------------------------|-----------|-----------|
| Example 31 | 99 : 1.0 : 0                         | 140                            | 0.52      | 0.57      |
| Control 20 | 99 : 1.0 : 0                         | 200                            | 1.2       | 3.51      |
| Control 21 | 99 : 0 : 1.0                         | 100                            | 1.2       | 3.51      |

#### Claims

1. A surface-roughened film of a composition (I) containing 97 to 99.99 wt. % of a thermoplastic polyester resin (a) and 0.01 to 3 wt.% of a thermoplastic resin (b) having a glass transition temperature higher than

that of said thermoplastic polyester resin (a), a critical surface tension which differs by more than 0.1 dyne/cm from that of said thermoplastic polyester resin (a), a melt viscosity at a temperature of 280°C and shear rate of  $10^2 \text{ sec}^{-1}$ , of 50 to 5000 Pas (500 to 50,000 poise), said film having microprotuberances cored with said thermoplastic resin (b) on a surface of said film.

- 5 2. A film according to claim 1, wherein the three dimensional center plane average roughness (SRa) of said surface film is from 0.005 to 0.05  $\mu\text{m}$ , and the three dimensional ten point average roughness (SRz) is from 0.06 to 0.4  $\mu\text{m}$ .
- 10 3. A film according to claim 1 which is of a composition (II) containing 96.9 to 99.9899 wt. % of said thermoplastic polyester resin (a), 0.01 to 3 wt. % of said thermoplastic resin (b) and 0.0001 to 0.1 wt. % of particles of an inorganic compound (c) having an average particle size of 0.2 to 4.0  $\mu\text{m}$ .
4. A film according to claim 3, wherein said inorganic compound (c) is silica.
- 15 5. A film according to claim 3 or 4, wherein the three dimensional center plane average roughness (SRa) of said surface is from 0.007 to 0.07  $\mu\text{m}$ , and the three dimensional ten point average roughness (SRz) is from 0.1 to 0.5  $\mu\text{m}$ .
- 20 6. A film according to any one of claims 1 to 5 wherein said thermoplastic resin (b) is an amorphous nylon, a maleimide copolymeric resin or an amorphous polyolefin.
7. A film according to any one of claims 1 to 6 wherein the refractive index of said thermoplastic resin (b) is from 1.45 to 1.68.
- 25 8. A film according to any one of claims 1 to 7 wherein the mean dispersed particle size of said thermoplastic resin (b) is from 0.01 to 1.0  $\mu\text{m}$ .
9. A laminate comprising at least one surface-roughened film as claimed in any one of the preceding claims, with said surface on an outer surface of the laminate, and at least one film of another polymer.
- 30 10. A laminate according to claim 9 wherein said another polymer is a thermoplastic polyester resin.
11. A method for fabricating a surface-roughened film as claimed in any one of claims 1 to 8 which comprises drawing an undrawn film of a composition (I) or (II) by at least 1.5X in at least one direction at a temperature between the glass transition temperatures of the resins (a) and (b).
- 35 12. A method according to claim 11 wherein the drawing ratio is higher than 3X in both axial directions.

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# EUROPEAN SEARCH REPORT

Application Number

EP 92 30 5949

| DOCUMENTS CONSIDERED TO BE RELEVANT  |  |  |   |
|--|--|--|---|
| Category   | Citation of document with indication, where appropriate, of relevant passages  | Relevant to claim                                    | CLASSIFICATION OF THE APPLICATION (Int. Cl.5) |
| Y  | EP-A-0 398 075 (UNITIKA LTD.)<br>* the whole document *  | 1-12   | C08J5/18<br>C08L67/02                         |
| Y  | EP-A-0 203 604 (TEIJIN LIMITED)<br>* page 6, line 15 - page 10, line 2;<br>claims; table 1 *   | 1-12   |   |
| Y  | Section Ch, Week 8818, 28 March 1988<br>Derwent Publications Ltd., London, GB;<br>Class A23, AN 88-123730<br>& JP-A-63 068 659 (NIPPON SHOKUBAI KAGAKU<br>KOGYO CO., LTD.) 28 March 1988<br>* abstract * | 1-12   |   |
| A  | EP-A-0 312 616 (TORAY INDUSTRIES, INC.)<br>* page 14, line 34 - page 19, line 8;<br>claims *   | 1-5,9,10   |   |
|  |  |  | TECHNICAL FIELDS<br>SEARCHED (Int. Cl.5)      |
|  |  |  | C08J<br>G11B                                  |
| The present search report has been drawn up for all claims   |  |  |   |
| Place of search<br>THE HAGUE   |  | Date of completion of the search<br>09 NOVEMBER 1992 | Examiner<br>KAUMANN, E.K.-H.                  |
| <p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone<br/> Y : particularly relevant if combined with another document of the same category<br/> A : technological background<br/> O : non-written disclosure<br/> P : intermediate document</p> <p>T : theory or principle underlying the invention<br/> E : earlier patent document, but published on, or after the filing date<br/> D : document cited in the application<br/> L : document cited for other reasons<br/> &amp; : member of the same patent family, corresponding document</p> |  |  |   |

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